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Application of Rb/Sr Ratio in Paleo-climate Inversion

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ABSTRACT

In order to study the intensity of chemical weathering during the formation of sedimentary strata in the site profile, the evolution of climatic environment in the region where the site profile is located was revealed. The rubidium (Rb) and strontium (Sr) values in the rubidium (Rb) and strontium (Sr) were tested and analysed. The Rb/Sr ratio has become an ideal alternative indicator in the study of regional environmental evolution. The Rb value in the strata section of Zhongba site is low, and the average value (calculated based on 202 sample values) is only 80 g/g. The Sr value was higher, averaging 866 g/g. The average Rb/Sr ratio is 0.19.

INTRODUCTION

Since the quaternary period, the world has experienced many important climate changes, which had an important impact on the formation of modern climate and the formation and development of early human society. There are a variety of research methods for paleoclimate and paleo environment, among which geochemical parameters are one of the important indexes for the study of climate and environmental evolution. Rb and Sr elements are widely used in the study of paleo environmental changes due to their unique geochemical properties in the supergene environment (Chen et al. 2017). Rb is a typical dispersed element, which is mainly distributed in all kinds of rock-building minerals in the form of homogeneity in nature, rarely forming independent minerals. According to the geochemical characteristics of Rb^+, the ion radius is relatively large (147 PM), which is close to that of K^+(123 PM). Therefore, Rb is mainly dispersed in minerals containing K in the form of homogeneity and image in various rocks, such as biotite, muscovite and potash feldspar. In the process of supergene weathering, these minerals are decomposed and release Rb, and the released Rb is easily adsorbed by the clay rich in K, only a small part of it is transported or leached, which determines that Rb cannot have a very strong leaching migration during weathering into soil (Fei et al. 2017). Sr is also a typical dispersed element. The ionic radius (112 PM) of Sr2+ is between Ca^{2+}(99 PM) and K^+(123pm), and it is often found in calcite, plagioclase, potash feldspar, mica and other minerals as trace elements in nature. Since the geochemical behaviour of Sr^{2+} in the supergene environment is more similar to that of Ca^{2+}, it is easier to migrate with soil solution or surface water in the form of free Sr (mainly in the form of carbonate), resulting in a large amount of Sr in the formation being leached. The geochemical properties of Rb and Sr determines that the supergene geochemical behaviour not only has a certain degree of similarity, but also embodies the supergene geochemical behaviour of the differences between the two, although certain condition of climate environment both showed a different degree of leaching migration patterns, but the Sr leaching transference is higher than Rb (Oster et al. 2017).

The innovation of this paper is to select the typical section stratum of Zhongba site to test and analyse Rb, Sr and Rb/Sr ratio, and study the intensity of chemical weathering in the formation process of the sedimentary stratum of the site section, so as to reveal the climatic and environmental evolution of the area where the site section is located since the middle and late Holocene in the Three Gorges area of the Yangtze river.

EARLIER STUDIES

Rb/Sr ratio in the loess, paleosol and application in lake sediments in the early 1960s, western scholars through the study found that Rb/Sr ratio can reflect the parent rock weathering degree. Martin-Chivelet et al. (2017) applied theRb, Sr element to the loess in the study of ancient climate and lake sediments. The Rb/Sr ratio has become a regional climate environment evolution in the study of ideal alternative indicators. Rubidium (Rb) and strontium (Sr) are trace elements with obvious difference and connection in geochemical behaviour. Carlson et al. (2018) have carried out a more detailed study on the migration rules of Rb and Sr of various parent rocks under weathering conditions, pointing out that the Rb/Sr value reflects the weathering strength of the parent rocks. Mine et al. (2017) also conducted a preliminary study on the distribution of Rb/Sr value in the loess section of Luochuan and found that this ratio can clearly identify the paleosoil-stratigraphic unit. In recent years, Wu et al. (2017) have found that Rb, Sr and Rb/Sr ratios in typical loess profiles of Xiashu loess in the north of China and the lower reaches of the Yangtze river can more accurately reflect the change of paleoclimate environment, and they are ideal replacement indexes in the study of regional environmental evolution.

MATERIALS AND METHODS

Sample Collection

Samples in April 2003 from Zhongba site T02ZZIDT0102 out west wall, location 30°20'43"N, 108°01'37"E, at an altitude of 148 m, 12 m in the whole section thickness. The site is a subtropical humid monsoon region, the annual average temperature 18.2°C, annual precipitation 193 mm, distinct seasons, abundant rainfall, sunshine 787°C accumulated temperature (10°C or higher activity 5). A total of 202 samples were sampled from the section from the source soil layer to the surface soil layer at different intervals. Samples were collected and put into zip2lock polyethylene bag, sealed to prevent sample contamination (Lewis & Grunwald 2017).

Characteristics and Dating of Profile Sediments

It is difficult to divide Zhongba site into sections because of its various cultural layers and the complex relationship between relics, relics and strata. The dating of the cultural layer is under the guidance of professional archaeological researchers, and the use of the archaeological artefact ranking method is mainly based on the cultural artefacts unearthed in the field, such as pottery pieces, porcelain pieces, bricks and tiles, etc., to determine the upper and lower strata ages (Willmes et al. 2017). At the same time, 14C dating method was used to accurately date the culture-layer sections with buried ancient trees and carbon scraps collected, and the 14C dating results were basically consistent with the archaeological dating results (Table 1). Based on the characteristics of section sediments, such as colour and texture, as well as field studies, the section stratum is briefly divided into 12 layers from top to bottom, which are summarized as follows:

Layer 1: modern cultivated layer (0 ~ 0.5m), brown sandy loam, containing a small amount of root system.

Layer 2: disturbance layer of Ming and Qing dynasties (0.5 ~ 1.5m), red and yellow silty sand, containing a small number of small stones and pottery pieces.

Layer 3: Ming dynasty culture layer (1.5-2.4m), dark grey silty sand, with pottery pieces and charcoal chips.

Layer 4: Tang dynasty cultural layer (2.4 ~ 3.2m), red and brown silt, less inclusion.

Layer 5: cultural layer of Qin and Han dynasties (3.2 ~ 4.1m), greyish-brown silty sand, containing a large number of pottery pieces and small stones.

Layer 6: cultural layer of the warring states period (4.1 ~ 5.6m), grey-black clay, containing more ceramic pieces, see animal bones.

Layer 7: spring and autumn cultural layer (5.6 ~ 6.5m), silty clay, containing a small amount of pottery, gravel and a small amount of carbon chips.

Layer 8: western Zhou culture layer (6.5 ~ 8.2m), yellow and red silt, containing a large number of pottery pieces.

Layer 9: Shang dynasty culture layer (8.2 ~ 9.5m), grey-black clay, multi-ceramic pieces, charcoal chips and bones.

Layer 10: Xia dynasty cultural layer (9.5 ~ 10.1m), yellow-brown silty sand, containing a large number of pottery pieces.

Layer 11: late Neolithic age (10.1 ~ 11.5m), grey and black silty clay, many ceramic pieces, carbon chips, see buried ancient trees.

Layer 12: raw soil (11.5 ~ 12m), dark red silty sand, no inclusions

Sample Analysis

The samples were naturally air-dried at room temperature for 1 month. After removing impurities such as ceramic tablets and bones, about 5g of each sample was pre-ground to 200 mesh (particle size: 0.08mm) and pressed into round sheets (Masi et al. 2018). Rb and Sr contents were analysed in the Modern Analysis Centre of Nanjing University and tested by the VP-320 X-ray fluorescence spectrometer produced by Shimadzu, Japan. The results were controlled by GSS1(11 times) and GSD9(15 times) of national geochemical standard samples, and the relative deviation (RSD) and relative error (RE) were both less than 1%.

RESEARCH RESULTS

Table 1 lists the statistical results of Rb, Sr and Rb/Sr analyses. It can be seen that the Rb value in the strata section of Zhongba site is relatively low, and the average value (calculated according to 202 sample values, the same below) is only 80g/g. The Sr value was higher, averaging 866g/g. The average Rb/Sr ratio is 0.19. These values are obviously different from Rb values (90 ~ 110g/g), Sr values (90 ~ 200g/g) and Rb/Sr values (0.50 ~ 0.94) in Xiashu loess section of the lower reaches of the Yangtze river in China. Secondly, from the perspective of the variation range of Rb and Sr values, the Rb values in the whole section have a small change range (mean value: 57 ~ 114 g/g), the standard deviation is 19, and the coefficient of variation (CV) is 23%. Sr values varied widely (mean 151 ~ 1 667 g/g), with a standard deviation of 575 and a coefficient of variation of up to 66%. The average Rb/Sr ratio of each layer is between 0.03 and 0.75, and the change is also very obvious. This indicates that the climate environment in this region is unstable and the intensity of chemical weathering is significantly different (Lien et al. 2017).

Elements have different geochemical behaviours in the supergene environment. During chemical weathering, some alkali and alkaline earth metal elements are easy to migrate and leach out. The migration sequence of these elements is usually Na>Ca>Sr>Mg>K. Based on the content of these elements in sediments and related chemical parameters, the degree of chemical weathering can be traced to understand the natural environment, especially the climatic conditions. Both Rb and Sr are typical dispersing factors and seldom form independent minerals in nature. They mainly exist in rock-forming minerals in the form of homogeneity. The ionic radius of Rb (0.147nm) is similar to that of K(0.133nm), and is mainly dispersed in minerals containing K(white mica, biotite and potassium feldspar, etc.), while the ionic radius of Sr (0.113nm) is similar to that of Ca (0.099nm), so Sr is mainly found in calcium-bearing minerals (such as plagioclase, amphibole, pyroxene and carbonate minerals, etc.) (Izquierdo et al. 2017).

In the supergenetic environment, the order of mineral weathering is generally calcite > olivine > basic plagioclase > pyroxene > amphibole > acid plagioclase > biotite > potash feldspar > white mica > quartz, that is, the minerals containing Rb are more resistant to chemical weathering than minerals containing Sr. In fact, the change of Rb/Sr value in weathering profile mainly depends on the degree of Sr loss. In rainwater leaching process, due to the larger ionic radius Rb, strong adsorption properties, clay mineral adsorption and retention of in situ or close range migration, compared with ionic radii of Sr was mainly in the form of free surface water or groundwater, chemical weathering caused the separation of Rb and Sr, resulting in higher residual part of the Rb/Sr ratio. The value of Rb/Sr actually indicates the degree of leaching and reflects the amount of climatic rainfall. Generally speaking, under the condition of humid and hot climate, the precipitation is abundant, chemical weathering is strong, the leaching loss of Sr is high, and the Rb/Sr ratio is high; on the contrary, in dry and cold climate, the leaching loss of Sr is low, and the Rb/Sr ratio is low.

In addition, a series of studies in recent years have shown that the value of Rb/Sr can more sensitively reflect the change of paleoclimate environment. Low Rb/Sr ratio indicates the cold and dry period when winter monsoon prevails, and conversely, it indicates the warm and humid period when summer monsoon prevails. That is to say, the peak corresponds to a warm climate period, while the trough indicates a cold period, which may be a more accurate proxy for the study of environmental evolution than the susceptibility. At present, the research on climate and environment evolution of the Holocene in China has begun to take shape. At about 9 ~ 8kab.p. 7 ~ 4kab.p and about 3kab.p. But, plus the complex terrain of China, and in a season with complex spatio-temporal variability of east Asia within the scope

Table 1: Analysis and statistics of Rb, Sr content and Rb/Sr ratio in Zhongba site profile.

Profile layer	Depth/m	Sample number	Rb/μg·g-1 Range	mean	Sr/μg·g-1 Range	mean	Rb/Sr Range	mean
1	0~0.5	5	97~109	104	447~182	315	0.21~0.59	0.33
2	0.5~1.5	20	35~108	86	130~430	206	0.08~0.67	0.41
3	1.5~2.4	14	36~90	67	355~1467	620	0.04~0.21	0.11
4	2.4~3.2	11	41~88	57	615~1044	705	0.09~0.03	0.08
5	3.2~4.1	14	88~118	106	340~870	521	0.02~0.21	0.20
6	4.1~5.6	27	49~114	70	423~3117	1497	0.01~0.09	0.05
7	5.6~6.5	14	29~84	65	848~3132	1565	0.01~0.41	0.04
8	6.5~8.2	30	19~113	65	198~4058	1581	0.01~0.09	0.03
9	8.2~9.5	23	19~90	60	1000~3283	1667	0.01~0.08	0.04
10	9.5~10.1	10	64~90	74	840~1268	1067	0.05~0.21	0.07
11	10.1~11.5	26	67~120	94	139~947	511	0.07~0.64	0.18
12	11.5~12	8	108~119	115	146~154	152	0.70~0.86	0.75

of risk control system, which makes the Holocene climate environment evolution in China with relatively obvious regional differences, the east and west, north and south in the warm period, the medieval warm period and start-stop time and strength of the aspects such as the little ice age are obviously different.

According to the dating results of Zhongba site's cultural and archaeological dating (instrumental matching method) and the dating results of T02ZZIDT0102 exploration section (see Table 1), the chronology sequence of this section can be preliminarily established. Based on the vertical distribution of Rb and Sr contents and Rb/Sr ratio in the strata profile of Zhongba site (Figs. 1-3), this paper reveals that the climate and environment evolution in this region has undergone the following six stages, including four warm periods.

(1) The soil layer of Zhongba site is about 5.1 kab.p., belonging to the Holocene great warm period, which is equivalent to the late Neolithic age. At this time, human activities began to step on the stage of history. From 5.1 ~ 4.3 kaB. P., namely the section depth is about

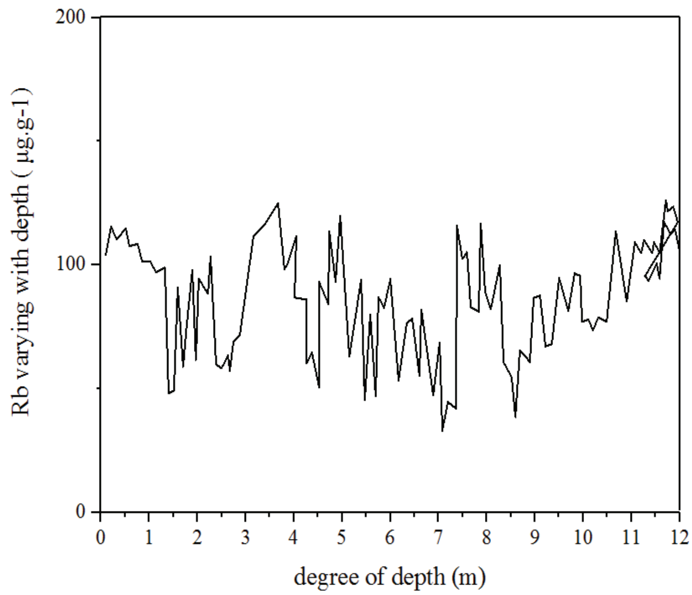

Fig. 1: Rb changes with depth.

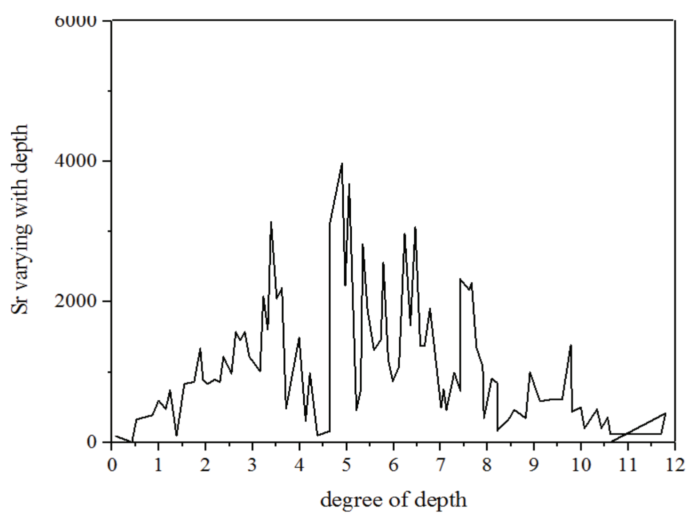

Fig. 2: Sr changes with depth.

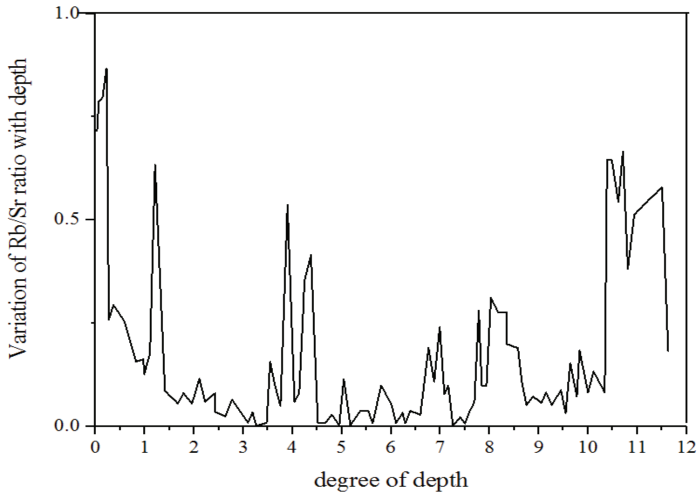

Fig. 3: Variation of Rb/Sr ratio with depth.

12.0 ~ 10.40 m (°C), this one phase, on the whole, for high temperature and rainy, unearthed a large number of potteries, animal bones and so on is a hot and humid climate condition at that time. The high content of sand and coarse sand in the sediments and the relatively low clay indicated that the flood was frequent. However, there was a significant mutation in the Rb/Sr curve near section 11m and 10.7m, that is, about 4.7kab.p. and 4.5kab.p. This shows that even in the Holocene warming period, the climate here is still unstable and fluctuating violently. This indicates that the cooling events in the Holocene warm period are universal in China.

(2) From the stratum 10.4m to 4.7m, that is, from 4.3 to 2.4kaB, only in the formation of 8.8 ~ 6.8 m (°C) near the rising temperatures (Monday) to (Rb/Sr ratio fluctuation is bigger, but the overall increase, while Rb and Sr content is higher), is about 3.4 ~ 2.8 kaB. P. to maintain a relatively warm period. The archaeological findings show that human beings started the salt production based on superior natural conditions, and gradually became the economic activity centre and important salt producing area of the Three Gorges region. However, there was a significant cooling process around the depth of 4.4m, or 2.9 kab.p., which should be the third phase of the new glacial period proposed by Denton et al.

(3) In section formation depth of 4.7 ~ 3.9 m (°C), roughly 2.4 ~ 2.1 kaB. P. (about the early warring states period to Qin and Han dynasties), the temperature is, the climate is appropriate, so that human activity is very frequent, and the phase of the formation of unearthed cultural relics, such as exposure of deep belly bottom cylinder, beam Angle of cup, lace neck won bottom tank and ZhuDong seems to also confirmed this point. However, at the depth of section 4.3m, that is, the time was about 2.3kab.p., the Rb/Sr ratio suddenly dropped rapidly, and there was an obvious temperature drop.

(4) In the formation 3.9 ~ 1.4m, the time is about 2.1 ~ 0.8 kab.p., the overall temperature is at the low stage, which is equivalent to the late Qin and Han dynasties to the late Ming dynasty in China. It can be seen that the high temperature and rainy climate during the Sui and Tang dynasties (1.5 ~ 1.1 kab.p.) was not obvious in this region.

(5) The formation depth of 1.5 ~ 1.4 m (°C), time is about 0.8 ~ 0.7 kaB. P., it is worth noting that the Rb/Sr ratio has a short and rapid rise, this may be in other areas in China is not very obvious reflection of medieval warm period.

(6) At the depth of 0.5m or more, about 600 ~ 500ab.p.(late Ming and early Qing), the temperature began to gradually decrease, which is generally known as the little ice age stage.

CONCLUSION

The Rb/Sr ratio was used to invert the change of paleoclimate and paleo-environment, which first began in the loess paleosol study, and then was widely used in the study of lake sediments and regional environmental archaeology. Many practices show that Rb/Sr ratio has become an ideal alternative indicator in the study of regional climatic and environmental evolution. But in both geology and archaeology study, the different occurrence conditions of Rb/Sr ratio refers to that the climate environment has a different degree of difference and Rb/Sr ratio in the process of specific research along with the soil magnetic susceptibility, sediment particle size, clay mineral, heavy mineral analysis and various environmental parameters recorded commonly used in paleoclimate and paleo-environment study, improve the science and accuracy.

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